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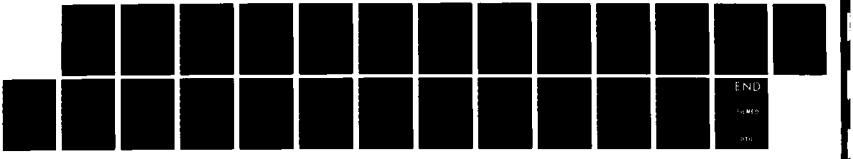

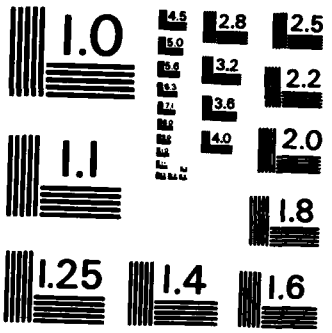

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Singlet oxygenation of (1-adamantylidene)ethyl acetate (4) and 6,6-dimethylcyclohex-1-enyl acetate (7) produces only "ene" reaction products. Photooxygenation of $\Delta^{1,6}$-2-oxabicyclo[4.4.0]decen-3-one (9), in contrast, yields ene, acyl-shifted, and [2+2]cycloaddition products. The product distribution resulting from oxidation of 9 indicates that attack of singlet oxygen ($^1O_2$) occurs exclusively on the same side of the double bond as the ester functional group. The bimolecular rate constant for reaction

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of 9 with $^1O_2$ is found to be ca. 50 times larger than those of 4 and 7. These results are explained most economically by invoking the initial formation of perepoxide intermediate. In the case of 9, stabilization of the transition state leading to the perepoxide by interaction of the incoming $^1O_2$ molecule with the ester functionality produces the observed rate enhancement and stereospecificity.

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Reactions of Singlet Oxygen with Enol Esters

by

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University of Illinois

Urbana, Illinois 61801

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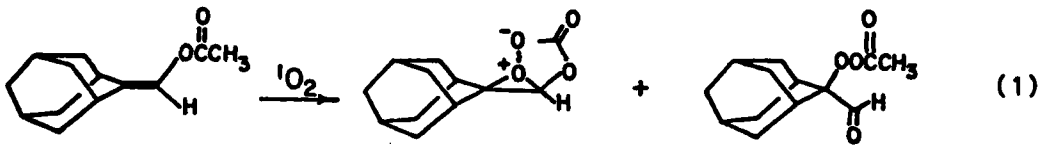
Singlet oxygen ($^1O_2$, $^1\Delta_g$) reacts with monoolefins to give either a dioxetane by [2+2]cycloaddition or an allylic hydroperoxide by the $^1O_2$ "ene" reaction.[1] The elucidation of the mechanism for these transformations has proven to be a challenging problem. Many of the tools available to chemists have been brought to bear, but there is still disagreement about the details of the reaction coordinate. Some experiments have been interpreted in favor of a concerted reaction,[2] while others are believed to support a stepwise processes involving perepoxide,[3] zwitterion,[4] biradical,[5] or reversibly formed exciplex[6] intermediates. To some extent, these differences of opinion may reflect the diversity of the olefinic systems studied.

We have previously reported that the reaction of $^1O_2$ with enol ester 1 gives perester 3 by intramolecular migration of the acyl group[7] (eq. 1). This reaction



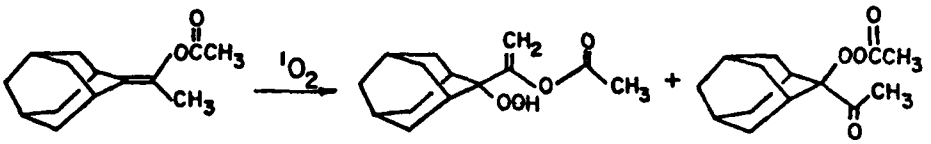
(1)

1 2 3

provides a mechanistic probe for the singlet oxygenation of olefins. Product and kinetic studies showed that the mechanism of the acyl-shift, the [2+2] cycloaddition, and the ene reactions are best described as proceeding through a common, polar intermediate most simply perceived as the perepoxide (2). We report herein experiments that further define the scope of the acyl-shift reaction and its use as a probe of singlet oxygenation in general.

Results

(1-Adamantylidene)ethyl Acetate (4). Singlet oxygenation of enol ester 4 is of interest because this olefin has the competing acyl group and abstractable allylic hydrogens on opposite sides of the double bond. Photooxygenation of 4 at room temperature in CS_2 using tetraphenylporphyrin (TPP) as the sensitizer gives the ene reaction product 5 in 88% yield. A minor product, tentatively identified as

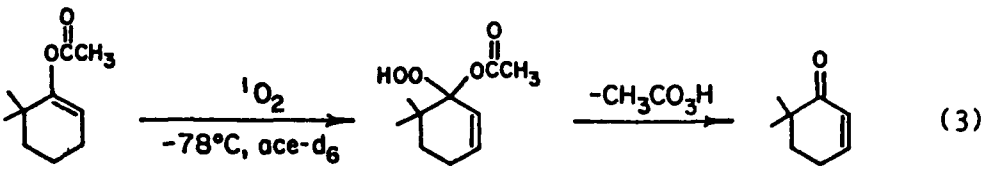


(2)

4 5 6

acyl-shift product 6, is observed spectroscopically in CS_2 (Eq. 2). All attempts to isolate this product, however, failed[8] (see Table I).

6,6-Dimethylcyclohex-1-enyl Acetate (7). Enol ester 7, which possesses competing groups in a trans relationship, was prepared to define further the acyl-shift competition with the ene reaction. The photooxygenation of 7 is sluggish, and only bleaching of the sensitizer occurs at room temperature. Prolonged irradiation at -78°C (methylene blue (MB) in acetone-d_6) does result in the oxidation of 7 by the ene pathway to form ene product 8 in quantitative yield (eq. 3, Table I).



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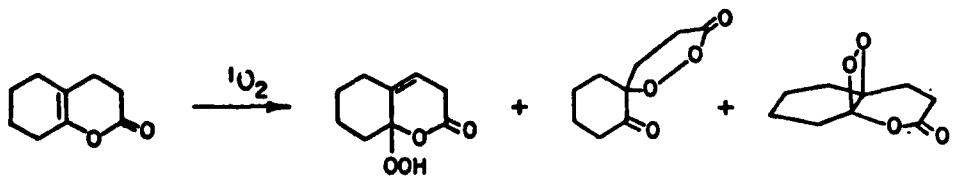
7 8

$\Delta^{1,6}$-2-Oxabicyclo[4.4.0]decen-3-one (9). The acyl group in enol lactone 9 is rigidly held in a favorable position with respect to the double bond for the acyl-shift reaction. Photooxygenation of 9 in a variety of solvents at -78° or 0°C leads to its very rapid consumption and the formation of ene (10), acyl-shift (11), and [2+2] cycloaddition (12) products (eq. 4). Peroxides 10 and 11 were fully



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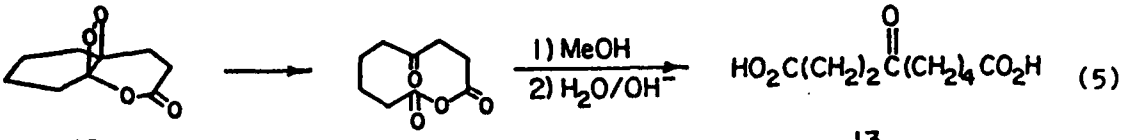
9 10 11 12

characterized by the usual methods after isolation. The formation of 12 was inferred from formation of diacid 13 after hydrolysis (eq. 5). It is important to note that the ene products that would be formed from the allylic hydrogens in the hydrocarbon ring are not detected (Table I).



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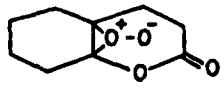
12 13

Kinetic Studies. The bimolecular rate constants for reaction of the enol esters with $^1O_2$ were determined. Two methods were employed. In the first, the rate of decay of the infrared phosphorescence characteristic of $^1O_2$ was monitored at various enol ester concentrations.[9] This gives k_q, the rate constant for all $^1O_2$ quenching processes (physical and chemical). The second method gives specifically the rate constant for the chemical reaction (k_r) by comparing relative rates of disappearance of the $^1O_2$ substrates during competitive photooxygenation.[10] In all cases studied, k_q and k_r are approximately equal. That is, the enol esters are not efficient physical quenchers of $^1O_2$. The results of the kinetic determinations are collected in Table 2. Of particular note is the rapid reaction of 9 in comparison with the other enol esters studied.

Discussion

As noted above, the previous investigation of the singlet oxygenation of enol esters provides evidence of the involvement of a common, polar intermediate in the ene, acyl-shift, and [2+2] cycloaddition reactions. A perepoxide intermediate provides the most straightforward explanation of the data. The present results support our earlier conclusions and permit a more detailed description of the reaction coordinate leading to the observed products.

The product distribution resulting from oxidation of enol lactone **9** is particularly interesting. Reaction occurs exclusively on the same side of the double bond as the ester functional group. A similar cis-directing effect has been observed previously with enol ethers.[11] Both perepoxide and zwitterion intermediates have been invoked in the explanation of this effect. Involvement of a perepoxide is supported by invoking stabilization of the transition state leading to that intermediate by interaction of the lone pair electrons on the oxygen of the enol ether with the LUMO of $^1O_2$.[12] Arguments favoring a zwitterion intermediate incorporate anomeric[13] or steric[14] effects. In the case of enol lactone **9**, involvement of perepoxide **14** provides the most economical explanation for the product distribution. It is difficult, for example, to account for formation of **10**, the major product, in terms of an open zwitterion intermediate.



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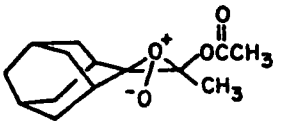
In contrast to **9**, no cis-directing effect is observed for enol acetate **4**. In this case, the major product results from allylic hydrogen abstraction opposite to the ester group. A possible reason for this is that the perepoxide **15** is formed in



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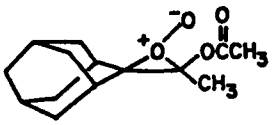
preference to the other isomer **16**. This explanation is suspect, however, since there is only a slight rate difference between **4** and **1** (Table 2), despite product distributions that are considerably different. A second possibility is that trapping of perepoxide **16** by the acyl group occurs slowly compared with its inversion to **15**. Although a zwitterion intermediate can be accomodated in this rationalization, the exclusive formation of **8** from enol acetate **7** seems inconsistent with the involvement of a zwitterion. To account for the exclusive formation of **8** via zitterion intermediates would require the more stable isomer, which cannot directly yield **8**, to be in rapid equilibrium with the other isomer, and the product-forming step to **8** to be the solely accessible product-producing pathway. In the only other study of photooxygenation of enol esters, Pusset and coworkers[15] report



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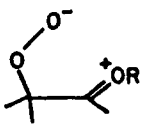
only formation of two isomeric ene products, in nearly equal amounts. This finding is also more consistent with a perepoxide than a zwitterion intermediate.

The rate constant for oxygenation of **9** is considerably greater than that for the other enol esters studied (Table 2). Apparently, locking the ester in a six-membered ring lowers the energy of the transition state leading to suspected perepoxide **14**. This may be due to a more favorable orientation of the oxygen lone

pair electrons for interaction with an incoming molecule of $^1O_2$ (vide supra). Alternatively, favorable orientation of the carbonyl group may allow stabilization of the developing negative charge in the nascent perepoxide.

The product distribution from photooxygenation of 9 is virtually independent of solvent. This is in contrast to the dramatic solvent effect observed previously in the photooxygenation of 1.[7] In the earlier case, we interpreted the result in terms of hydrogen bonding interactions of the perepoxide with the solvent. In the present case, the favorable orientation of the carbonyl group may provide intramolecular stabilization of the perepoxide making hydrogen bonding less effective. In contrast, enol ethers exhibit a pronounced solvent-polarity effect.[3b,16] Also, solvent-incorporation products are obtained from photooxidation of enol ethers in methanol.[4b,16] These types of products are not observed for the enol esters. This is reasonably due to the difference in the stability of potential



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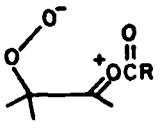

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zwitterion intermediates (17 and 18) resulting from these precursors. The zwitterion derived from the ether (17) is expected to be the more stable of the two because of the superior electron-donating ability of the ether functionality.[17]

Photooxygenation of enol ethers and enol esters also respond very differently to temperature. A large effect is observed in the product distribution of enol ethers.[16] We observe no temperature dependence for enol esters (e.g., see 9, Table 1). In this respect, enol esters behave very similarly to unsaturated

hydrocarbons.[18] The observation that the product ratio is not a function of temperature implies that there are negligible differences in $\Delta H^{\neq}$ for formation of the various products. In other words, the magnitude of $\Delta S^{\neq}$ determines the product ratio. Negligible differences in $\Delta H^{\neq}$ seem reasonable for a high energy intermediate such as the perepoxide. The magnitude of $\Delta H^{\neq}$ for product formulation is likely to be small in all cases. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ that we obtain for the rate determining step (Table 2) are similar to those reported for simpler ene reactions.[9b]

Conclusions

Reaction of $^1O_2$ with enol esters possessing abstractable allylic hydrogens generally proceeds by the ene pathway. If, however, the ester functionality is included in a six-membered ring, favorable orientation of the carbonyl group permits the acyl-shift reaction to compete effectively with allylic hydrogen abstraction. The involvement of the ester group of the enol lactone in the stabilization of the transition state of the rate-limiting step is implicated by the large rate enhancement observed. The reaction of $^1O_2$ with enol esters shows no Markovnikov directing effects and no formation of alcohol-incorporation products in methanol solution; product distribution is insensitive to solvent polaritiy or temperature change. These findings contrast with those reported for enol ethers, suggesting a difference in mechanism which is understood by assuming that a 1,4-zwitterion may be an energetically accessible intermediate for enol ethers, but not enol esters. The involvement of a perepoxide intermediate in the reaction of $^1O_2$ with enol esters accounts for the results in a straightforward manner.

Experimental Section

General. THF and DME were distilled from sodium under a N_2 atmosphere, using benzophenone ketyl as indicator. Acetic anhydride was fractionally distilled, with the first 10% of the distillate being discarded. All other commercially available reagents were used without further purification.

Photooxygenations were performed using either a 250 W, 24 V Sylvania tungsten-halogen projector lamp or a 400 W General Electric Lucalox sodium lamp. NMR tubes (5 and 10 mm) were used as the photooxygenation vessels. The tubes were irradiated within a windowed Dewar maintained at the indicated temperature. Oxygen was passed through a drying tube containing anhydrous $CaSO_4$ and molecular sieves, bubbled through the solution being photooxygenated via a Teflon needle, and passed out of a bubbler filled with mineral oil. The outside of the upper portion of the NMR tubes was cooled with dry ice during photooxygenation to prevent solvent evaporation.

GC analyses were carried out on a Varian 3700 gas chromatograph equipped with a linear temperature programmer and a flame ionization detector. A Hewlett-Packard 5900 integrator was used for quantitative analyses. A 6 ft. x 0.125 in. glass column containing 5% SE-30 on Gas Chrom Q (100-120 mesh) was used for all GC analyses.

The method for determining k_r by monitoring the decay of $^1O_2$ phosphorescence has been described previously.[9b]

(1-Adamantylidene)ethyl Acetate (4). To a 50 mL round-bottom flask was added 2.17 g of 2-adamantyl methyl ketone,[19] 0.25 g of p-toluenesulfonic acid, and 10 mL of acetic anhydride. The flask was fitted with a magnetic stir bar and a distillation head, and the contents were heated at partial reflux so that 5 mL of distillate were collected over a 30 min period. An additional 10 mL of acetic anhydride were added and the mixture was again heated so that 10 mL of distillate were collected over a 45 min period. Addition and collection of another 10 mL portion of acetic anhydride were performed over another 45 min period. The

resulting mixture was poured into a flask containing 50 mL of ether and 50 mL of sat. $NaHCO_3$ solution. Solid sodium bicarbonate was added cautiously, with stirring, until a saturated solution was maintained. The resulting mixture was stirred for 30 min, decanted into a separatory funnel, and the layers separated. The ether layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residual oil was distilled (104°C, 1 mm) to yield 2.23g (83%) of 4 as a colorless oil. The distillate was crystallized from $MeOH/H_2O$: mp 34-35°C; ^1H NMR (CS_2) δ 1.63-1.99 (m, 12 H), 1.73 (s, 3H), 1.97 (s, 3H), 2.57 (bs, 2H); IR ($CHCl_3$) 1730, 1740 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.31; H, 9.17. Found: C, 75.98; H, 9.38.

6,6-Dimethylcyclohex-1-enyl Acetate (7). To a flame-dried 100-mL three-neck round-bottom flask fitted with an addition funnel and magnetic stir bar was added, under a N_2 atmosphere, 3.44 g (30 mmol, 35 wt.% dispersion, in mineral oil) of potassium hydride. The mineral oil was removed by washing with three 10 mL portions of pentane.[20] The residual pentane was removed under vacuum. To the resulting KH powder was added 5 mL of dry DME. A solution of 2.52 g (20 mmol) of 2,2-dimethylcyclohexanone[21] in 50 mL of DME was added dropwise to the stirring KH suspension over a 10 min period, and then stirred for an additional 20 min. The resulting enolate solution was transferred via cannula under N_2 to an addition funnel which was fitted to a 250 mL three-neck round-bottom flask containing 12.6 mL (150 mmol) of acetic anhydride. The enolate solution was added dropwise to the stirring acetic anhydride over a 20 min period, yielding a very viscous, cream-colored mixture. This mixture was poured into a flask containing 200 mL of ether and 200 mL of sat. $NaHCO_3$. Solid $NaHCO_3$ was added until a saturated solution was maintained, and the mixture was stirred for 15 min. The mixture was decanted into a separatory funnel and the layers were separated. The aqueous layer was washed with two 50 mL portions of ether. The ether solutions were combined, washed with water and then brine, dried over $MgSO_4$, filtered, and concentrated under

vacuum. The residual liquid was distilled (61-63°C, 1.7 mm), yielding 2.49 of the crude product. The crude product was fractionally distilled, using a Teflon spinning-band column, to yield 1.55 g of enol acetate 7 (88°C, 17 mm): 1.55-1.74 (m, 4H), 2.00 (s, 3H), 1.98-2.09 (m, 2H), 5.07 (t, 1H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.38; H, 9.60. Found: C, 71.27; H, 9.70.

$\Delta^{1,6}$-2-Oxabicyclo[4.4.0]decen-3-one (9).[22] A 3.00 g (17.6 mmol) quantity of 2-oxocyclohexanepropanoic acid was dissolved in 150 mL of acetic anhydride. The resulting solution was heated at reflux, under a N_2 atmosphere, for 5h. A 0.17 g (0.89 mmol) quantity of TsOH monohydrate was added and the mixture was heated at reflux for an additonal 1 h period. After cooling to room temperature, the acetic anhydride was removed by distillation at aspirator pressure. The resulting residue was taken up in 300 mL of ether. This ether solution was washed with two 100 mL portions of 5% $NaHCO_3$, followed by 100 mL of brine, dried over $MgSO_4$, filtered, and concentrated under vacuum, to yield 2.54 g of crude 9 as a dark oil. Pure 9 was obtained by flash chromatography[23] (silica gel, 20% EtAc/hexane), followed by Kugelrohr distillation (115°C, 0.7 mm), as a colorless oil (1.90 g, 71%): ^1H NMR ($CDCl_3$) δ 1.55-1.85 (m, 4H), 1.98-2.34 (m, 6H), 2.62 (t, 2H); IR (neat) 1713, 1765 cm^{-1}. Anal. Calcd for $C_9H_{12}O_2$: C, 71.01; H, 7.96. Found: C, 70.81; H, 8.06.

Keto Diacid 13. To a 25 mL three-neck round-bottom flask equipped with a gas dispersion tube, Teflon stopcock-protected septum inlet, and magnetic stir bar was added 159 mg (105 mmol) of enol lactone 9 and 7 mL of methanol. The flask was cooled to -78°C and ozone was bubbled through the solution. The addition of ozone was continued for 5 min after the solution became blue. The solution was then purged with N_2 for 5 min and 0.20 ml (2.7 mmol) of dimethyl sulfide was added. The solution was stirred for 5 min and then allowed to warm to room temperature. After stirring at room temperature for 3 h, the solution was concentrated under vacuum. The residual oil was combined with 15 mL of 2 N NaOH and the resulting solution heated at reflux for 4 h. After cooling to room temperature, the solution was

diluted with 25 mL of water and washed with two 20 mL portions of ether. The resulting aqueous layer was acidified to pH≤1 with 6 N HCl and extracted with five 30 mL portions of ether. The combined ether extract was dried over $MgSO_4$, filtered, and concentrated under vacuum to yield 51 mg of crude **13** as a light tan solid. This material was recrystallized ($CHCl_3$): mp 106-107°C (lit.[24] 108.5-109.5); ^1H NMR (ace-d_6) δ 1.60 (quintet, 4H), 2.30 (t, 2H), 2.46-2.61 (m, 4H), 2.72 (t, 2H).

Photooxygenation of **4**-Isolation of Ene Product **5**. A 0.22 g (1.0 mmol) quantity of **4** was combined with 2 mL of a saturated solution of methylene blue in acetone-d_6 and photooxygenated, using the tungten-halogen lamp, for 1 h. The resulting mixture was dissolved in 15 mL of ether. The ether solution was washed with two 5 mL portions of water and one of brine, dried over $MgSO_4$, filtered, and concentrated under vacuum to yield 0.22 g of crude **5** as a yellow oil. Hexane (0.50 mL) was added to the oil, and the resulting solution was cooled to -15°C to crystallize **5** as slightly yellow crystals: mp 89-92°C; ^1H NMR (CS_2) δ 1.48-1.88 (m, 12H), 2.14 (s, 3H), 2.16 (bs, 2H), 5.05 (d, 1H), 5.16 (d, 1H), 8.65 (s, 1H); IR (CS_2) 3370, 1740 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 8.01. Found: C, 67.05; H, 8.02.

Photooxygenation of **7**. To a 5 mm NMR tube was added 14.2 mg (0.0845 mmol) of enol acetate **7**, 0.60 mL of acetone-d_6 saturated with methylene blue, and 0.050 mL (4.83 μmol, 0.0966 M, in $CDCl_3$) of a solution of *p*-dichorobenzene (as an internal standard). The enol acetate was photooxygenated, using the sodium lamp, at -78°C for 10 h. The resulting solution was peroxidic, as indicated by a positive strch-iodide test. The solution was analyzed by ^1H NMR spectroscopy: Enol acetate **7** (64% recovered); Enone **8**[25] δ 1.06 (s, 6H), 1.83 (t, 2H), 2.35-2.47 (m, 2H), 5.80 (d of t, 1H), 6.96 (d of t, 1H), 44% (based on starting material), 108% (Based on recovered starting material); Acetic acid δ 1.96 (by addition of authetic acetic acid).

Photooxygenation of 9-Isolaton of Ene Product **10**. A 141 mg (0.928 mmol) quantity of enol lactone **9** was combined with a 5 x 10^{-4} M solution of TPP in CS_2 and photoxygenated for 1 hr at -78°C, using the sodium lamp. During this time crude **10** precipitated as a green solid. The resulting mixture was filtered rapidly, and the collected solid was washed with two 2 mL portions of CS_2 which had been cooled to -78°. This process yielded 81 mg of crude **10**. Repeated recrystallization (CH_2Cl_2/CS_2) yielded **10** as light green crystals (the green is due to a TPP by-product, white **10** was obtained by chromatography): mp 92-93°C; ^{1}H NMR (CD_3OD) δ 1.23-1.92 (m, 4H), 2.16-2.50 (m, 4H), 3.10 (d of d, 2H, J_1=3.49 Hz, J_2=2.86 Hz[26]), 5.71 (d of t, 1 H, j_1=3.49 Hz, J_3=1.91 Hz); ^{13}C NMR ($CDCl_3$) δ 22.3, 25.9, 30.1, 31.3, 35.3, 108.5, 118.5, 132.7, 170.7; IR ($CDCl_3$) 1734 cm^{-1}. Anal. Calcd for $C_9H_{12}O_4$: C, 58.68; H, 6.58. Found: C, 58.55; H, 6.59. Peroxide titer 99% of theory.

Photooxygenation of **9** - Isolation of Peroxylactone **11**. A 537 mg (3.53 mmol) quantity of enol lactone **9** was combined with 3 mL of acetone-d_6 which had been saturated with methylene blue, and was photooxygenated, using the sodium lamp, at -78°C for 3 h. The resulting solution was combined with 417 μL (3.53 mmol) of trimethyl phosphite at -78°C under a N_2 atmosphere. This mixture was stirred for 15 min and warmed to room temperature. The resulting solution was dissolved in 100 mL of ether and washed with two 30 mL portions of 5% $NaHCO_3$. The ether solution was washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum to yield 155 mg of an oily residue. This material was chromatographed (Chromatotron 1 mm silica gel plate, 33% EtAc/hexane) and recrystallized (EtAc/hexane) to yield 96 mg of **11** as white crystals: mp 65.5-66.5°C; ^{13}C NMR ($CDCl_3$) δ 22.6, 23.6, 27.3, 36.1, 36.6, 37.9, 108.4, 173.0, 174.7; IR ($CDCl_3$) 1744, 1803 cm^{-1}. Anal. Calcd for $C_9H_{12}O_4$: C, 58.68; H, 6.58. Found: C, 58.84; H, 6.59. Peroxide titer 91% of theory (**11** reacts with NaI very slowly, 24 h were required).

Photooxygenation of 9 - Isolation of Keto Diacid 13. A 105 mg (0.691 mmol) quantity of enol lactone 9 was combined with a solution of methylene blue (ca. 10^{-4} M) in MeOH and photooxygenated, using the sodium lamp, at -78°C for 2 h. The photooygenation mixture was dissolved in 30 mL of ether, and the resulting ether solution was extracted with two 10 mL portions of 5% $NaHCO_3$. The combined $NaHCO_3$ extracts were acidified with 6 N HCl and extracted with three 10 mL portions of ether. The combined ether extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residual oil was chromatographed (Chromatotron 1 mm silica gel plate, 1% AcOH in EtAc/hexane (3:1)) to yield 20 mg of a monoester of 13. This material was dissolved in 1 mL of 2 N NaOH and this solution heated at 110°C for 1 h. After cooling to room temperature, the solution was acidified with 6 N HCl and extracted with three 15 mL portions of ether. The combined ether extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum to yield 9 mg of an off-white solid. This material has identical spectral properties as authentic keto diacid 13.

Determination of Photooxygenation Product Yields. Unless otherwise indicated, yield determinations were performed on 0.50 mL portions of enol ester solutions (ca. 0.2 M), photooxygenated for 30 min, using the sodium lamp.

Yields of acyl-shift product 11 were determined by GC (injector=180°C; oven=3 min at 130°C, and then 10°C/min to 200°C; He=30 ml/min), using tridecane and hexadecane as internal standards. For a given photooxygenation solvent and temperature, at least three independent determinations were made; the reproducibility among independent runs was ± 5%.

The yields of ene products 5 and 10 were determined by NMR, by comparison of the integrals of the vinyl hydrogen resonances with those of the internal standard, p-dichlorobenzene. Enol acetate 4 was photooxygenated for 1 h, using the tungten-halogen lamp for determination of the yield of 5. For 10, at least three independent determinations were made for a given photooxygenation temperature and

solvent; the reproducibility among independent runs was ± 3%. For photooxygenation of **10** in CS_2 solution, the mixture was combined with 0.50 ml of acetone-d_6 before analysis to dissolve the precipitated **10**.

The yield of the [2+2]cycloaddition product **12** were determined by NMR spectorscopy from the integral of the methoxy resonance (3.61 δ) of the monoester (ME) of **13**, using p-dichlorobenzene as the internal standard. For photooxygenation in MeOH, the reaction mixture was kept at room temperature for 2 h, the resulting solution was concentrated under vacuum, and the residue was dissolved in acetone-d_6 for analysis. For photooxygenation in CS_2, the reaction mixture was dissolved in 0.50 mL of ether and then added to 3 mL of MeOH, after which, the above procedure for photooxygenation in MeOH was followed. For photooxygenation in acetone-d_6 at -78°C, the reaction mixture was immediately poured into 5 mL of MeOH, and the above analysis procedure performed. For photooygenation at 0° in acetone-d_6, the enol lactone was photooxygenated for 5 min and then immediately poured into 5 mL of MeOH, after which the analysis procedure was performed.

Determination of k_r by Competitive Photooxygenation. The relative rate constants (k_A/k_B) of two $^1O_2$ substrates (A and B), when photooxygenated competitively, were determined using the relationship $k_A/k_B = \ln([A]_0/[A]_t)/\ln([B]_0/[B]_t)$.[10] Enol acetate **1** was photooxygenated in competition with 2-methyl-2-pentene (2M2P). The relative rate of disappearance of **1** and 2M2P was determined by integration of the vinyl hydrogens in the NMR spectra of these compounds with p-dichlorobenzene as an internal standard. The value of k_r for **1** was calculated using the value of k_r for 2M2P reported by Manring and Foote.[10a] The value of k_r for **7** was determined in the same manner by competition with **1**. The value of k_r for **9** was determined by its competitive photooxygenation with 2M2P. After photooxygenation, the mixture was reduced with an excess of Ph_3P and analyzed by GC (injector=220°C; oven=3 min at 40°C, and then 15°C/min to 200°C; He=30 ml/min), using tridecane as an internal standard. In this way, the disappearance of **9** and the appearance of the two photooxygenation products of 2M2P (P_1 and P_2) were

followed. Using the relationship $\ell n([2M2P]_0/[2M2P]_t) = \ell n\{[P_1+P_2]_f/([P_1+P_2]_f-[P_1+P_2]_t)\}$ (where $[P_1+P_2]_f$ = concentration of the sum of the products after complete conversion of 2M2P), the relative rate constants were determined by plotting $\ell n\{[P_1+P_2]_f/([P_1+P_2]_f-[P_1+P_2]_t)\}$ vs. $\ell n\ ([9]_0/[9]_t)$. The response factors of P_1 and P_2 were determined by taking 2M2P to complete conversion and using the values reported by Manring and Foote for P_2/P_1.[10a] The value of k_r for **9** was then calculated from the reported value of k_r of 2M2P.[10a]

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Table 1. **Product Yields for Photooxygenation of Enol Esters 4, 7, and 9**

Enol Ester	Solvent/Sens.	Temp.(°C)	Ene (% Yield)	Acyl-Shift	[2+2]
4	CS_2/TPP	23	5 (88)	6 (7)?	--
7	ace-d_6/MB	-78	8 (108)	--	--
9	CS_2/TPP	0	10 (67)	11 (24)	12 (9)
9	CS_2/TPP	-78	10 (64)	11 (34)	12 (8)
9	ace-d_6/MB	0	10 (56)	11 (29)	12 (12)
9	ace-d_6/MB	-78	10 (56)	11 (33)	12 (13)
9	CD_3OD/MB	0	10 (62)	11 (22)	12 (16)
9	CD_3OD/MB	-78	10 (61)	11 (22)	12 (14)

Table 2. **Rate Constants (k_r) for the Reaction of the Enol Esters with $^1O_2$ in Acetone-d_6.**

Enol Esters	Temp.(°C)	$10^{-4}k_r$ ($s^{-1}M^{-1}$)	$\Delta H^{\neq}$(kcal/mol)	$\Delta S^{\neq}$(eu)
1	23	3.4[a]		
1	23	2.7[b]		
4	23	4.5[a]		
7	23	0.8[b]		
9	23	100[b]	1.1	-31
9	-32	55[b]		
9	23	108[a]		

[a]Determined by monitoring the decay of $^1O_2$ phosphorescence following laser flash photolysis at various enol esters concentrations.

[b]Determined by competitive photooxygenation.

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